CLAIMS

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WHAT IS CLAIMED IS:

- 1. A medical article comprising an implantable substrate having a coating, the coating including a polymeric product of a reaction between a first reagent, a second reagent, and a third reagent, wherein:
- (a) the first reagent is selected from a group consisting of compounds having formulae (1), (2), (3), and (4):

O O
$$\| \| \| \| \|$$
 HO- R_2 -C-NH-Y-NH-C- R_2 -OH

HO-X-OH (3)

$$H_2N-Y-NH_2 \tag{4}$$

(b) the second reagent is selected from a group consisting of compounds having formulae (5), (6), (7), and (8):

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$$\parallel$$
 \parallel \parallel \parallel (6) \parallel HO- R_2 -C-NH- R_4 -NH-C- R_2 -OH

$$HO-R_4-OH$$
 (7)

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$$H_2N-R_4-NH_2$$
 (8)

(c) the third reagent is a dicarboxylic acid having the formula (9):

O O
$$\| \| \|$$
 HO—C—R₃—C—OH

wherein:

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R₁ is hydrogen, methyl, iso-propyl, sec-butyl; iso-butyl, or benzyl group;

R₂ is methylene, methylene, *n*-propylene, *iso*-propylene, ethylmethylene, *n*-butylene, *iso*-butylene, *sec*-butylene, or *n*-amylene group;

 R_3 is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

R₄ is a moiety derived from a compound selected from a group consisting of poly(ethylene glycol), poly(propylene glycol), random poly(ethylene glycol-co-propylene glycol), poly(ethylene glycol)-block-poly(propylene glycol), hyaluronic acid, poly(2-hydroxyethyl methacrylate), poly(3-hydroxypropylmethacrylamide), poly(styrene sulfonate), poly(vinyl pyrrolidone), and cellulosics;

X is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12; and

Y is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is 1, 2, or 5.

- 2. The medical article of Claim 1, wherein the implantable substrate is a stent.
- 3. The medical article of Claim 1, wherein the compound of formula (1) is a dioldiamine, the diol-diamine is a product of condensation of an amino acid and a diol.
 - 4. The medical article of Claim 3, wherein the amino acid has the formula (10):

 H_2N — CHR_1 —COOH. (10)

- 5. The medical article of Claim 3, wherein the amino acid is selected from a group consisting of glycine, alanine, valine, isoleucine, leucine, and phenyl alanine.
- 6. The medical article of Claim 3, wherein a diol is selected from a group consisting of ethylene glycol, 1,3-propanediol, 1,4-butane diol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, and 1,12-dodecanediol.
 - 7. The medical article of Claim 1, wherein the compound of formula (2) is an amidediol, the amidediol is a product of condensation of a hydroxy acid and a diamine.
- 10 8. The medical article of Claim 7, wherein the hydroxy acid has the formula (11):

 HO—R₂—COOH. (11)
 - 9. The medical article of Claim 7, wherein the hydroxy acid is selected from a group consisting of glycolic acid, lactic acid, β -hydroxybutyric acid, α -hydroxyvaleric acid, and ϵ -hydroxycaproic acid.
 - 10. The medical article of Claim 7, wherein the diamine is selected from a group consisting of putrescine, 1,2-ethanediamine, and cadavarene.
 - 11. The medical article of Claim 1, wherein the compound of formula (3) is selected from a group consisting of ethylene glycol, 1,3-propanediol, 1,4-butane diol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, and 1,12-dodecanediol.

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- 12. The medical article of Claim 1, wherein the compound of formula (4) is selected from a group consisting of putrescine, 1,2-ethanediamine, and cadavarene.
- 13. The medical article of Claim 1, wherein the compound of formula (5) is a PEG-diester-diamine conjugate, the conjugate is a product of condensation of an amino acid and poly(ethylene glycol).
 - 14. The medical article of Claim 13, wherein the amino acid has the formula (10):

 H₂N-CHR₁-COOH. (10)
- The medical article of Claim 13, wherein the amino acid is selected from a group consisting of glycine, alanine, valine, isoleucine, leucine, phenyl alanine, tyrosine,
 serine, and glutamic acid.
 - 16. The medical article of Claim 1, wherein the compound of formula (6) is a PEG-amidediol conjugate, the conjugate is a product of condensation of a hydroxy acid and PEG-diamine.
 - 17. The medical article of Claim 16, wherein the hydroxy acid has the formula (11):

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$$HO-R_2-COOH$$
. (11)

- 18. The medical article of Claim 17, wherein the hydroxy acid is selected from a group consisting of glycolic acid, lactic acid, β -hydroxybutyric acid, α -hydroxyvaleric acid, and ϵ -hydroxycaproic acid.
- 19. A medical article comprising an implantable substrate having a coating, the coating including a copolymer having a general formula (12) or (13):

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$$-[M-P]_m-[M-Q]_n-$$
 (12)

$$-[M_1-P]_p$$
 (13)

wherein:

M is a moiety represented by the structure having the formula (14)

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$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
-C-R_2-C-
\end{array} \tag{14}$$

P is a moiety selected from a group consisting of structures having the formulae (15),

10 (16), (17), and (18):

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$$-0-X-0-$$
 (17)

$$20 -NH-Y-NH-$$
 (18)

Q is a moiety selected from a group consisting of structures having the formulae (19), (20), and (21)

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M₁ is a moiety represented by the structure having the formula (22):

R₁ is hydrogen, methyl, iso-propyl, sec-butyl; iso-butyl, or benzyl group;

R₂ is methylene, methylene, n-propylene, iso-propylene, ethylmethylene, n-butylene, iso-butylene, sec-butylene, or n-amylene group;

 R_3 is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

X is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

Y is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is 1, 2, or 5;

Z is a moiety derived from a compound selected from a group consisting of poly(ethylene glycol), poly(propylene glycol), random poly(ethylene glycol-co-propylene glycol), poly(ethylene glycol)-block-poly(propylene glycol), hyaluronic acid, poly(2-hydroxyethyl methacrylate), poly(3-hydroxypropylmethacrylamide), poly(styrene sulfonate), poly(vinyl pyrrolidone, and cellulosics; and

m, n, and p are integers where the value of m is between 5 and 1,800, the value of n is between 1 and 800 and the value of p is between 4 and 1,500.

20. The medical article of Claim 19, wherein the polymer is selected from a group consisting of copolymers of formulae (23), (24), (25), (26), (27), (28), (29), (30), (31), (32), (33), (34), (35), (36), (37), (38), (39), (40), (41), (42), and (43):

(23)

$$\begin{bmatrix} O & O & CH_3 & O & CH_3 \\ -C - CH_2 \end{bmatrix}_{2}^{-1} C - NH - CH - C - O - CH_2 \end{bmatrix}_{4}^{-1} O - C - CH - NH \\ - C - CH_2 \end{bmatrix}_{2}^{-1} C - NH - CH - C - O - PEG_{300} - O - C - CH - NH \\ - C - CH_2 \end{bmatrix}_{2}^{-1} C - NH - CH - C - O - PEG_{300} - O - C - CH - NH \\ - C - CH_2 \end{bmatrix}_{0.47}^{-1} C - NH - CH_2 - C - CH_3 \\ - C - CH_2 \end{bmatrix}_{2}^{-1} C - NH - CH_2 - C - CH_3 \\ - C - CH_3 - CH_$$

(24)

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(25)

(26)

(27)

$$\begin{bmatrix} O & O & CH_3 & O$$

(28)

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(30)

$$\begin{bmatrix}
O & O & O & O & CH_3 & O & O & CH_3 \\
C & CH_2 & C & O & CH_2 & C & CH_2 &$$

5 (34)

$$= \begin{bmatrix} O & O & CH_3 & O & O & CH_3 \\ \parallel & \parallel & \parallel & \parallel & \parallel & \parallel \\ C - (CH_2)_4 & C - NH - CH - C - O - (CH_2)_4 & O - C - CH - NH \\ \end{bmatrix}_{0.37} \begin{bmatrix} O & O & CH_3 & O & O & CH_3 \\ \parallel & \parallel & \parallel & \parallel & \parallel \\ C - (CH_2)_4 & C - NH - CH - C - O - PEG_{300} - O - C - CH - NH \\ \end{bmatrix}_{0.67}$$

5 (40)

(41)

(42)

(43)

- A method for fabricating a medical article, the method including synthesizing a copolymer and forming a coating based on the copolymer on at least a portion of an implantable substrate, the synthesizing of the copolymer including reacting a first reagent with a second reagent and with a third reagent, wherein:
- (a) the first reagent is selected from a group consisting of compounds having formulae (1), (2), (3), and (4):

15 O O
$$\| \| \| \|$$
 (2)

$$HO-X-OH$$
 (3)

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$$H_2N-Y-NH_2$$
 (4)

(b) the second reagent is selected from a group consisting of compounds having formulae (5), (6), (7), and (8):

$$HO-R_4-OH$$
 (7)

$$H_2N-R_4-NH_2 \tag{8}$$

(c) the third reagent is a dicarboxylic acid having the formula (9):

wherein:

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R₁ is hydrogen, methyl, *iso*-propyl, *sec*-butyl; *iso*-butyl, or benzyl group;

R₂ is methylene, methylmethylene, *n*-propylene, *iso*-propylene, ethylmethylene, *n*-butylene, *iso*-butylene, *sec*-butylene, or *n*-amylene group;

 R_3 is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

R₄ is a moiety derived from a compound selected from a group consisting of poly(ethylene glycol), poly(propylene glycol), random poly(ethylene glycol-co-propylene glycol), poly(ethylene glycol)-block-poly(propylene glycol), hyaluronic acid, poly(2-hydroxyethyl methacrylate), poly(3-hydroxypropylmethacrylamide), poly(styrene sulfonate), poly(vinyl pyrrolidone), and cellulosics;

X is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

Y is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is 1, 2, or 5.

- 5 22. The method of Claim 21, wherein the implantable substrate is a stent.
 - 23. The method of Claim 21, wherein the molar ratio between the first reagent, the second reagent, and the third reagent is about 1:1:2.
 - 24. The method of Claim 21, wherein the compound of formula (1) is a dioldiamine, the diol-diamine is a product of condensation of an amino acid and a diol.
- 10 25. The method of Claim 24, wherein the amino acid has the formula (10): H₂N-CHR₁-COOH. (10)
 - 26. The method of Claim 24, wherein the amino acid is selected from a group consisting of glycine, alanine, valine, isoleucine, leucine, and phenyl alanine.
- 27. The method of Claim 24, wherein a diol is selected from a group consisting of ethylene glycol, 1,3-propanediol, 1,4-butane diol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, and 1,12-dodecanediol.
 - 28. The method of Claim 21, wherein the compound of formula (2) is an amidediol, the amidediol is a product of condensation of a hydroxy acid and a diamine.
- 20 29. The method article of Claim 28, wherein the hydroxy acid has the formula (11):

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$$HO-R_2-COOH.$$
 (11)

- 30. The method of Claim 28, wherein the hydroxy acid is selected from a group consisting of glycolic acid, lactic acid, β -hydroxybutyric acid, α -hydroxyvaleric acid, and ϵ -hydroxycaproic acid.
- 5 31. The method of Claim 28, wherein the diamine is selected from a group consisting of putrescine, 1,2-ethanediamine, and cadavarene.
 - 32. The method of Claim 21, wherein the compound of formula (3) is selected from a group consisting of ethylene glycol, 1,3-propanediol, 1,4-butane diol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, and 1,12-dodecanediol.
 - 33. The method of Claim 21, wherein the compound of formula (4) is selected from a group consisting of putrescine, 1,2-ethanediamine, and cadavarene.
 - 34. The method of Claim 21, wherein the compound of formula (5) is a PEG-diester-diamine conjugate, the conjugate is a product of condensation of an amino acid and poly(ethylene glycol).
 - 35. The method of Claim 34, wherein the amino acid has the formula (10):

 H₂N-CHR₁-COOH. (10)
 - 36. The method of Claim 34, wherein the amino acid is selected from a group consisting of glycine, alanine, valine, isoleucine, leucine, phenyl alanine, tyrosine, serine, and glutamic acid.

- 37. The method of Claim 21, wherein the compound of formula (6) is a PEG-amidediol conjugate, the conjugate is a product of condensation of a hydroxy acid and PEG-diamine.
 - 38. The method of Claim 37, wherein the hydroxy acid has the formula (11):

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$$HO-R_2-COOH$$
. (11)

- 39. The method of Claim 37, wherein the hydroxy acid is selected from a group consisting of glycolic acid, lactic acid, β -hydroxybutyric acid, α -hydroxyvaleric acid, and ϵ -hydroxycaproic acid.
- 40. A method for fabricating a medical article, the method including synthesizing a copolymer and forming a coating based on the copolymer on at least a portion of an implantable substrate, wherein the copolymer has a general formula (12) or (13):

$$-[M-P]_m-[M-Q]_n-$$
 (12)

$$-[M_1-P]_p$$
 (13)

wherein:

M is a moiety represented by the structure having the formula (14)

$$\begin{array}{cccc}
O & O \\
\parallel & \parallel \\
-C-R_3-C-
\end{array} \tag{14}$$

P is a moiety selected from a group consisting of structures having the formulae (15), (16), (17), and (18):

$$R_1$$
 O O R_1 | | (15)

5 O O
$$\| \| \| \|$$
 (16) $-O-R_2-C-NH-Y-NH-C-R_2-O-$

$$-O-X-O-$$
 (17)

$$-NH-Y-NH-$$
 (18)

Q is a moiety selected from a group consisting of structures having the formulae (19), (20), and (21)

 M_1 is a moiety represented by the structure having the formula (22):

R₁ is hydrogen, methyl, *iso*-propyl, *sec*-butyl; *iso*-butyl, or benzyl group;

R₂ is methylene, methylmethylene, n-propylene, iso-propylene, ethylmethylene, n-butylene, iso-butylene, sec-butylene, or n-amylene group;

 R_3 is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

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X is a straight chained or branched aliphatic alkylene group C_nH_{2n} , wherein n is an integer between 2 and 12;

 $\label{eq:Y} Y \mbox{ is a straight chained or branched aliphatic alkylene group C_nH_{2n}, wherein n is 1, 2, or 5; and$

Z is a moiety derived from a compound selected from a group consisting of poly(ethylene glycol), poly(propylene glycol), random poly(ethylene glycol-co-propylene glycol), poly(ethylene glycol)-block-poly(propylene glycol), hyaluronic acid, poly(2-hydroxyethyl methacrylate), poly(3-hydroxypropylmethacrylamide), poly(styrene sulfonate), poly(vinyl pyrrolidone, and cellulosics; and

m, n, and p are integers where the value of m is between 5 and 1,800, the value of n is between 1 and 800 and the value of p is between 4 and 1,500.

41. The method of Claim 40, wherein the copolymer is selected from a group consisting of copolymers of formulae (23), (24), (25), (26), (27), (28), (29), (30), (31), (32), (33), (34), (35), (36), (37), (38), (39), (40), (41), (42), and (43):

(23)

$$\begin{bmatrix} O & O & CH_3 & O & CH_3 \\ C & CH_2 \end{bmatrix}_{2}^{2} C - NH - CH - C - O + CH_2 \end{bmatrix}_{4}^{2} O - C - CH - NH$$

$$\begin{bmatrix} O & O & CH_3 & O & CH_3 \\ C & CH_2 \end{bmatrix}_{2}^{2} C - NH - CH - C - O - PEG_{300} - O - C - CH - NH \end{bmatrix}_{0.47}^{2}$$

$$(24)$$

$$\begin{bmatrix} CH_{3}-CH-CH_{3} & CH_{3}-CH-CH_{3} \\ O & O & CH_{2} & O & O & CH_{2} \\ -C-CH_{2} & C-NH-CH-C-O-CH_{2} & O-C-CH-NH \\ -C-CH_{2} & C-NH-PEG_{600}-NH \\ -C-C$$

$$\begin{bmatrix} CH_3-CH-CH_3 & CH_3-CH-CH_3 \\ O & O & CH_2 & O & O & CH_2 \\ C-CH_2 & C-NH-CH-C-O & CH_2 & O & CH-NH & C-CH-NH & C-CH-O \\ O & O & CH_2 & C-NH-CH-C-O & CH_2 & C-O-CH-C-NH-PEC_{600} & NH-C-CH-O \\ O & O & CH_3 & O & O & CH_3 \\ C-CH_2 & C-NH-CH-C-O & CH_2 & C-O-CH-C-NH-PEC_{600} & NH-C-CH-O \\ O & O & CH_3 & O & O & CH_3 \\ O & O & CH_3 & O & O \\ O & O & CH_3 & O \\ O & O &$$

$$\begin{bmatrix} O & O & CH_3 & O & O & CH_3 \\ O & O & CH_3 & O & O & CH_3 \\ C - C - CH - C - NH - CH_2 - NH - C - CH - O - M - C - CH - O - M - CH_2 - CH_3 \\ O & O & CH_2 & O & O & CH_3 \\ C - CH_2 - CH_2 - CH_3 - CH_$$

$$\begin{bmatrix}
O & O & CH_3 & O & O & CH_3 \\
C & CH_2 + C & O - CH - C - NH + CH_2 + NH - C - CH - O + M + C - CH - O$$

$$\begin{bmatrix}
O & O & CH_3 & O & CH_3 \\
C & CH_2 & C & O & CH & C & CH & CH_2 \\
C & CH_2 & C & O & CH & C & CH & C & CH & O
\end{bmatrix}
\begin{bmatrix}
O & O & CH_3 & O & CH_3 \\
C & CH_2 & C & CH & C & CH & O
\end{bmatrix}
\begin{bmatrix}
O & O & CH_3 & O & CH_3 \\
C & CH_2 & C & CH & C & CH_2 \\
R & C & C & CH_2 & R & C & CH_2
\end{bmatrix}$$
(30)

(32)

$$\begin{array}{c|c}
\hline
O & O \\
\Box & \Box & \Box \\
C & \Box & \Box & \Box \\
\hline
C & \Box & \Box & \Box \\
C & \Box & \Box &$$

5 (37)

$$\begin{bmatrix}
O & O & CH_3 & O & O & CH_3 \\
II & II & II & II & II \\
C - PEG_{1000} - C - O - CH - C - NH + CH_2 + NH - C - CH - O + II
\end{bmatrix}_{n}$$
(39)

$$= \begin{bmatrix} O & O & CH_3 & O & O & CH_3 \\ \parallel & \parallel & \parallel & \parallel & \parallel & \parallel \\ C-(CH_2)_{4} & C-NH-CH-C & -O-(CH_2)_{4} & O-C-CH-NH \\ \end{bmatrix}_{0.37} \begin{bmatrix} O & O & CH_3 & O & O & CH_3 \\ \parallel & \parallel & \parallel & \parallel & \parallel & \parallel \\ C-(CH_2)_{4} & C-NH-CH-C & -O-PEG_{300} & O-C-CH-NH \\ \end{bmatrix}_{0.67}$$

(40)

. (4

(42)

(43)